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Serial No. 414,223

Filing Date 29 September 1989

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AD-D014 313

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1           IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
2                           APPLICATION FOR LETTERS PATENT

3           ALLOYING OF METALS FOR CORROSION RESISTANCE

4                           SPECIFICATION

5                           BACKGROUND OF THE INVENTION

6           FIELD OF THE INVENTION:

7           This invention relates, in general, to corrosion inhibition,  
8           and, more specifically, to a method of forming corrosion resistant  
9           bulk metals.

10          DESCRIPTION OF THE BACKGROUND ART:

11          Aqueous corrosion is a major problem in the performance and  
12          durability of metals in many applications. It has been found that  
13          many transition metals and their alloys, such as aluminum alloys,  
14          have good uniform resistance to corrosion because of the formation  
15          of a protective passive oxide film. However, the major corrosion  
16          problem with such metals is the localized breakdown of this passive  
17          oxide film. This breakdown leads to the initiation and growth of  
18          corrosion pits.

19          The breakdown of the passive oxide film and subsequent pitting  
20          of metals can be partially explained in terms of surface charge  
21          characteristics of the metal oxide/solution interface. To cause  
22          pitting, an ion (such as chloride) must first adsorb at the metal  
23          oxide/solution interface before penetration or dissolution through  
24          the oxide film to locally attack the underlying metal.

1           The adsorption characteristics of an oxide-covered metal  
2 surface depend on the net surface charge of the metal. An  
3 important parameter controlling this surface charge is the pH of  
4 zero charge of the oxide. The pH of zero charge of the oxide ( $\text{pH}_{\text{pzc}}$ )  
5 is the pH of a solution at which the surface oxide in such solution  
6 has a net zero charge. In general, whether or not a given oxide-  
7 covered metal such as aluminum is subject to corrosive attack in  
8 a given aqueous environment will depend on the relative values of  
9  $\text{pH}_{\text{pzc}}$  of the metal oxide, the pH of the solution and the charge of  
10 the attacking species. "The Effect of pH of Zero Charge on the  
11 Pitting Potential," Jour. Electr. Soc., Vol. 133, No. 5, (May  
12 1986).

13           Various techniques have been used to combat the adsorption of  
14 ions and subsequent corrosion of such metals. It has been found  
15 that localized corrosion resistance of metals such as aluminum can  
16 be improved by conventional alloying techniques wherein an alloy  
17 is selected wherein the  $\text{pH}_{\text{pzc}}$  of the alloy's oxide inhibits  
18 anion/cation adsorption. However, conventional alloying techniques  
19 are limited by two considerations. First, alloying additions are  
20 normally based on strength considerations, but the resulting  
21 intermetallic phases generally disrupt the passive oxide film and  
22 are detrimental to corrosion resistance. Second, most alloying  
23 elements known to improve corrosion properties have a limited  
24 solubility in many metals, such as aluminum.

1           An alternative to conventional alloying which has been used  
2 is ion implantation, a process by which virtually any element can  
3 be introduced into the surface of any solid material to selected  
4 depths and concentrations by means of a beam of high velocity ions  
5 (usually tens to hundreds of kiloelectron volts) striking a target  
6 mounted in a vacuum chamber. The surface alloys produced by ion  
7 implantation can be tailored to have enhanced properties with  
8 regards to wear, catalysis or aqueous corrosion.

9           The bombarding ions lose energy in collisions with substrate  
10 electrons and atoms. Penetration depths of tens to thousands of  
11 angstroms are achieved before incident ions lose all their energy  
12 and stop in the solid. The maximum concentration of implanted  
13 atoms is generally located beneath the substrate surface. The  
14 surface concentration of implanted ions that can be achieved can  
15 vary in samples receiving the same apparent implantation dose from  
16 extremely dilute alloys to 50 atomic per cent alloys. Natishan,  
17 P. M., McCafferty, E., and G. K. Hubler. "Surface Charge  
18 Considerations in the Pitting of Ion-Implanted Aluminum," Journal  
19 Elect. Chem. Soc. 135, 321 (1988). Thus, ion implantation suffers  
20 from major drawbacks as a method of improving corrosion resistance  
21 because it is not possible to predict the corrosion protection  
22 afforded by various alloys and because serious corrosion problems  
23 still persist with ion implantation.

1 Ion beam mixing has also been used to increase corrosion  
2 protection in some metals. Recent studies show, however, that both  
3 ion beam mixing and ion implantation produce similar results for  
4 palladium-implanted titanium, a self-passivating metal, both  
5 reducing corrosion rates by a factor of about 500 - 1000. "Review.  
6 Naval Research Laboratory Surface Modification Program: Ion beam  
7 and Laser Processing of Metal Surfaces for Improved Corrosion  
8 Resistance," Mat. Sci. Engin. 86 (1987) 1-17.

9 What is needed is a method for improving the corrosion  
10 resistance of metals, such as aluminum. To date, no such method  
11 exists for metals that are not self-passivating.

12 SUMMARY OF THE INVENTION

13 Accordingly, it is an object of this invention to improve the  
14 corrosion resistance of metals.

15 It is also an object of this invention to inhibit the  
16 corrosion of a metal without altering the desired bulk properties  
17 of the metal.

18 It is also an object of this invention to provide a method of  
19 producing a corrosion resistant metal.

20 These and other objects are accomplished by implanting a  
21 corrosion-resistant species into the surface of a bulk metal. The  
22 selected corrosion-resistant species is implanted into the bulk  
23 metal to a depth of at least about 50 angstroms such that the  
24 resulting surface will form an oxide layer. The oxide layer is

1 composed of at least about three percent oxide of the corrosion-  
2 resistant species.

3 DESCRIPTION OF THE PREFERRED EMBODIMENT

4 It has been found that not all corrosion-resistant species  
5 implant well into various metal substrates and that not all  
6 combinations of species/substrates result in corrosion resistant  
7 surfaces. The following table lists the combinations of bulk  
8 metals and implanted corrosion-resistant species that would offer  
9 sufficient resistance to corrosion when the corrosion attack is by  
10 anions.

11	<u>SUBSTRATE</u>	<u>IMPLANTED SPECIES</u>
12	Al	Sb, W, V, Mo, Si, Ta, Nb, Mn,
13		Zr, U, Ru, Ir, Pd, Ti, Pb, Co,
14		Cr, Sn, Sc, Hg, Ce, Pr, Ni, Th,
15		Fe, Pu, Y
16	Fe	Sb, W, V, Mo, Si, Ta, Nb, Mn,
17		Zr, U, Ru, Ir, Pd, Ti, Pb, Co,
18		Cr, Sn, Sc, Hg, Ce, Pr, Ni, Th
19	Mg	Sb, W, V, Mo, Si, Ta, Nb, Mn,
20		Zr, U, Ru, Ir, Pd, Ti, Pb, Co,
21		Cr, Sn, Sc, Hg, Ce, Pr, Ni, Th,
22		Fe, Pu, Y, Al, Bi, Cu, Zn, La,
23		Be, Cd
24	Cu	Sb, W, V, Mo, Si, Ta, Nb, Mn,
25		Zr, U, Ru, Ir, Pd, Ti, Pb, Co,
26		Cr, Sn, Sc, Hg, Ce, Pr, Ni, Th,
27		Fe, Pu, Y, Al, Bi
28	Zn	Sb, W, V, Mo, Si, Ta, Nb, Mn, Zr,
29		U, Ru, Ir, Pd, Ti, Pb, Co, Cr,

1 Sn, Sc, Hg, Ce, Pr, Ni, Th, Fe,  
2 Pu, Y, Al, Bi, Cu

3 In the most preferred embodiment, the substrate is Al and the  
4 corrosion-resistant species is Mo.

5 The following table lists the combinations of bulk metals and  
6 implanted corrosion-resistant species that would offer the most  
7 improved resistance to corrosion when the corrosion attack is by  
8 cations.

9	<u>SUBSTRATE</u>	<u>IMPLANTED SPECIES</u>
10	Si	Ta, Nb, Mn, Zr, U, Ru, Ir, Pd,
11		Ti, Pb, Co, Cr, Sn, Sc, Hg, Ce,
12		Pr, Ni, Th, Fe, Pu, Y, Al, Bi,
13		Cu, Zn, La, Be, Cd, Mg
14	Ta	Mn, Zr, U, Ru, Ir, Pd, Ti, Pb,
15		Co, Cr, Sn, Sc, Hg, Ce, Pr, Ni,
16		Th, Fe, Pu, Y, Al, Bi, Cu, Zn,
17		La, Be, Cd, Mg
18	Nb	Mn, Zr, U, Ru, Ir, Pd, Ti, Pb,
19		Co, Cr, Sn, Sc, Hg, Ce, Pr, Ni,
20		Th, Fe, Pu, Y, Al, Bi, Cu, Zn,
21		La, Be, Cd, Mg
22	Zr	U, Ru, Ir, Pd, Ti, Pb, Co, Cr,
23		Sn, Sc, Hg, Ce, Pr, Ni, Th, Fe,
24		Pu, Y, Al, Bi, Cu, Zn, La, Be,
25		Cd, Mg
26	Sn	Sc, Hg, Ce, Pr, Ni, Th, Fe, Pu,
27		Y, Al, Bi, Cu, Zn, La, Be, Cd,
28		Mg

29 In the most preferred embodiment, the substrate is Si and the  
30 corrosion-resistant species is Al.

1           Whether or not corrosion attack is by anions or cations, the  
2 bulk metals can be alloys of the above listed substrates. In such  
3 a case, the corrosion-resistant species listed would be applicable  
4 for the alloys of the named elements. Furthermore, combinations  
5 of the corrosion-resistant species may be used for the invention.

6           It has been found that the above bulk metals do exhibit  
7 corrosion resistance to varying degrees. However, the present  
8 invention offers a method of improving the corrosion resistance  
9 which was previously unattainable.

10           The top 50 angstroms of the metal surface has been found to  
11 be important to the continued corrosion resistance of the  
12 aforementioned bulk metals. A mixture of corrosion-resistant  
13 species and bulk metal is formed directly on the surface of the  
14 bulk metal to a depth of at least about 50 angstroms. Preferably,  
15 the thickness is between about 50 and 10,000 angstroms. The amount  
16 of corrosion-resistant species implanted into the bulk metal must  
17 be an amount such that an oxide layer will form that is at least  
18 3 percent oxide of the corrosion-resistant species. An oxide layer  
19 of at least about 3 percent oxide of the corrosion-resistant  
20 species and no more than about 95 percent oxide of the corrosion-  
21 resistant species is preferable, since some corrosion-resistant  
22 species, while offering corrosion resistance at these percentages,  
23 may actually encourage corrosion at higher percentages. Most

1 preferably, the oxide layer contains from about 5 percent to about  
2 50 percent of the oxide of the corrosion-resistant species.

3 The remaining composition of the layer consists of oxide of  
4 the bulk metal. The formation of this oxide layer results in  
5 greater corrosion protection for the underlying bulk metal than is  
6 available with current methods. Therefore, the amount of  
7 corrosion-resistant species implanted into the bulk metal should  
8 preferably be an amount such that the oxide layer has an effective  
9 amount of oxide of the corrosion-resistant species, an effective  
10 amount defined as the amount of oxide giving the corrosion  
11 protection afforded by the invention.

12 Any means of implanting the corrosion-resistant species  
13 described above into the bulk metal such that a metal surface with  
14 the above described properties is formed may be used. The means  
15 giving the most consistent results is ion beam mixing. Ion beam  
16 mixing is carried out in the following manner.

17 One or more layers of corrosion-resistant species are  
18 deposited on the bulk metal, thick enough to form an effective  
19 metal surface as described above. If the layer of deposited  
20 corrosion-resistant species is too thin, it will not be possible  
21 to get a metal surface of proper concentration that will, in turn,  
22 form an effective layer of oxide. Therefore, the preferred  
23 thickness of the deposited layer is in the range from about 100Å  
24 to 300Å. The most preferred thickness of the layer is about 150Å.

1           It should be noted that more than one layer can be deposited  
2 on the bulk metal so that the metal surface need not be a binary  
3 mixture. In fact, one can produce a ternary, quaternary, etc.  
4 mixture. The corrosion-resistant species described above to be  
5 implanted into the substrate can be in any form that will allow  
6 the formation of a metal surface with the above described  
7 properties on the bulk metal. Preferably, the layer is a sputter-  
8 deposited, electrodeposited or evaporated film or an ion implanted  
9 layer. Several alternating layers of thin films can be deposited  
10 to produce a ternary, quaternary, etc. mixture. These layers may  
11 be deposited by sputter-deposition, electrodeposition or  
12 evaporation.

13           Any inert or chemically reactive ion can be used as a  
14 bombardment agent to ion beam mix the corrosion-resistant species  
15 into the bulk metal. The energy can be adjusted according to the  
16 molecular weight of the particular ion used and the penetration of  
17 the ion into the film and substrate required. Preferably, the  
18 energy level is in the range of between about 110 keV and 1.8 MeV.

19           The ion is selected according to the corrosion application,  
20 i.e., so that it should not cause galvanic effects. The ion is  
21 selected from rare gases, metals, rare earths, lanthanides and  
22 actinides. Preferably, the ion is selected from the group of  
23 argon, xenon, ions of the material of the substrate and ions of the  
24 layers of deposited film. Most preferably, the ion is xenon.



1 potentials were determined potentiostatically by stepping the  
 2 potential in 25 to 50 mV increments from the corrosion potential  
 3 in the anodic direction. Before the onset of pitting, steady state  
 4 currents at each step were reached in 5 to 20 minutes. But when  
 5 pitting occurred, the current increased steadily with time at that  
 6 potential (the "pitting potential") and at more positive  
 7 potentials. At potentials below (less positive than) the pitting  
 8 potential, pits do not initiate. Above the pitting potential, pits  
 9 initiate and grow. Therefore, a higher (more positive) pitting  
 10 potential represents an improved resistance to pitting attack.  
 11 The results below show that the various ion beam mixed Mo-Al  
 12 surface alloys demonstrate an improved resistance to pitting  
 13 corrosion.

14	<u>DEPOSITION</u>	<u>MIXING CONDITIONS</u>	<u>DOSE</u>	<u><math>E_{PIT}</math> (V)</u>	<u><math>\Delta E_{PIT}^*</math> (V)</u>
15			(x 10 <sup>6</sup> ions/cm)		
16	None	None	-	-0.700	-
17	Ion				
18	implantation**	None	-	-0.525	+0.175
19	(20 atomic %)				
20	Ion				
21	implantation**	Xe <sup>++</sup> , 250keV	2.5	-0.400	+0.300
22	(20 atomic %)				
23	Ion				
24	implantation**	Xe <sup>++</sup> , 1.8MeV	2.6	-0.050	+0.650
25	(20 atomic %)				
26	Vapor				
27	deposition	None	-	-0.650	+0.050
28	(270Å)				

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1	Vapor				
2	deposition	Xe <sup>++</sup> , 250keV	3.5	-0.600	+0.100
3	(300Å)				
4	Vapor				
5	deposition	Cr <sup>+</sup> , 110keV	3.0	-0.050	+0.650
6	(150Å)				
7	Sputter				
8	deposition	None	-	-0.650	+0.050
9	(100Å)				
10	Sputter				
11	deposition	Mo <sup>+</sup> , 120keV	1.0	-0.600	+0.100
12	100Å)				

13 \*Compared to pure, unalloyed aluminum

14 \*\*The actual surface concentration for the Mo-Al implanted samples  
15 was 1-2 atomic percent.

16 The pitting potentials for the various ion beam mixed Mo-  
17 al surface alloys were 100 to 650 mV more positive than that of  
18 pure aluminum. Moreover, the pitting potentials of the ion beam  
19 mixed surface alloys were also more positive than those for the  
20 corresponding unmixed alloys, i.e., either Mo-implanted or Mo-  
21 coated aluminum.

22 RBS profiles before and after ion beam mixing for the sample  
23 implanted with 20% Mo and then mixed with Xe<sup>++</sup> at 1.8 MeV show that  
24 ion beam mixing causes the Mo to move further into the bulk and  
25 also caused an increase in the oxide film thickness. Samples  
26 prepared from vapor deposited Mo coatings showed similar results.

EXAMPLE II

Measurement of oxide film thicknesses before and after ion beam mixing showed that ion beam mixing at moderate to high energies (0.25-1.8 MeV) produced an increase in the thickness of the aluminum oxide film.

As-polished aluminum, ion-implanted aluminum, and ion-implanted samples that were subsequently ion beam mixed were compared relative to their surface oxygen concentration and their oxide thicknesses. Results for ion implanted samples with nominal surface concentrations of 4 and 12% Mo are also listed. The table shows that the thickness of the oxide films on as-polished aluminum and the as-implanted surface alloys produced at lower doses were similar, but that the oxide film thickened considerably at higher doses. The thickness of the oxide film on a Mo(20)Al surface alloy also increased during ion beam mixing with 250 keV and 1.8 MeV xenon.

SURFACE OXYGEN CONCENTRATIONS AND OXIDE THICKNESSES

	<u>10<sup>15</sup> ATOMS/CM<sup>2</sup></u>	<u>A*</u>	<u>E<sub>pIT</sub>** (V)</u>
Al	24	34	-
Mo(4)Al	24	34	+0.140
Mo(12)Al	28	39	+0.155
Mo(20)Al	64	90	+0.175
Mo(20)Al before mixing with 250 KeV Xenon	60	84	+0.175
Mo(20)Al after mixing with 250 KeV Xenon	71	99	+0.300

1	Mo(20)Al before mixing	46	64	+0.175
2	with 1.8 MeV Xenon			
3	Mo(20)Al after mixing	88	123	+0.650
4	with 1.8 MeV Xenon			

5 \* $10 \times 10^{15}$  atoms/cm<sup>2</sup> corresponds to 14Å of Al<sub>2</sub>O<sub>3</sub>.  
6 \*\*Compared to pure, unalloyed aluminum

7 Thus, in terms of the effect on oxide film thicknesses, ion  
8 beam mixing at high doses comprises an ion beam anodization  
9 technique which serves to thicken the oxide film on aluminum  
10 without the necessity of conventional chemical or electrochemical  
11 treatments in aqueous solutions. A nonporous compact film can be  
12 produced without contamination from the aqueous solution.

13 The table shows the largest increases in pitting potential  
14 were obtained for the surface alloys prepared by ion beam mixing  
15 with 0.25 to 1.8 MeV, xenon, i.e., for those surface alloys having  
16 the thickened oxide film. These results are unique in that  
17 previous work in the literature reports that the pitting potential  
18 of aluminum alloys in 0.1M KCl is independent of oxide film  
19 thickness for thickness up to 1300 Å for aluminum alloys anodized  
20 by conventional techniques employing aqueous solutions [Z. A.  
21 Foroulis and M. J. Thubrikar, J. Electrochem. Soc., 122, 1296  
22 (1975)].

EXAMPLE III

Ion beam mixed binary Cr-Al surface alloys having improved resistance to pitting attack were produced as follows. The aluminum substrate was prepared as described in Example I. Chromium films were prepared by sputter cleaning the aluminum substrate with argon ions and then by sputter depositing 100 Å of Cr onto the substrate. The sample was then ion beam mixed using the conditions listed below.

<u>DEPOSITION</u>	<u>MIXING CONDITIONS</u>	<u>DOSES</u> (x 10 <sup>16</sup> ions/cm <sup>2</sup> )	<u>E<sub>pII</sub></u> (V)	<u>ΔE<sub>pII</sub>*</u> (V)
None	None	-	-0.700	-
Sputter deposition Cr(100Å)	None	-	-0.600	+0.100
Sputter deposition Cr(100Å)	Cr <sup>+</sup> , 120 keV	1	-0.575	+0.125

\*Compared to pure, unalloyed aluminum.

The pitting potential for the Cr-Al ion beam mixed surface alloy was 0.125 V higher than that of pure Al and 0.025 V higher than for the sample which contained a sputter deposited Cr coating which was not ion beam mixed. In addition, the Cr-Al surface alloy retains the advantage of obviating adhesion problems associated with coatings.

EXAMPLE IV

Ion beam mixed ternary Mo-Cr-Al surface alloys having improved resistance to pitting attack were produced as follows. The aluminum substrate was prepared as described in Example I. Chromium and molybdenum films were prepared by sputter cleaning the surface on an aluminum substrate, and sputter depositing 100Å of molybdenum and then 100 Å of chromium onto the substrate. The sample was then ion beam mixed using the conditions described below.

<u>DEPOSITION</u>	<u>MIXING CONDITIONS</u>	<u>DOSES</u> (x 10 <sup>16</sup> ions/cm <sup>2</sup> )	<u>E<sub>pII</sub></u> (V)	<u>ΔE<sub>pII</sub>*</u> (V)
None	None	-	-0.700	-
Ion implantation Cr(12a/o)+Mo(4a/o)	None	-	-0.585	0.115
Sputter deposition Cr(100Å)+Mo(100Å)	None	-	-0.600	+0.100
Sputter deposition Cr(100Å)+Mo(100Å)	Cr <sup>+</sup> , 120 keV	1	-0.575	+0.125

\*Compared to pure, unalloyed aluminum.

The pitting potential of the Mo-Cr-Al ion beam mixed surface alloy was 0.100 V higher than pure Al, 0.025 V higher than Al with a sputter deposited coating of Cr and Mo, and comparable to that of a Cr-Mo-Al surface alloy prepared by ion implantation. Both the ion implanted and ion beam mixed surface alloys carry the advantage of precluding adhesion problems associated with coatings.



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ABSTRACT

→ The corrosion resistance of bulk metals is improved by implanting a corrosion-resistant species into the surface of the bulk metal in a layer beginning at the surface and extending to a depth of at least about 50 angstroms. An amount of corrosion-resistant species is deposited so that the oxide layer that forms on the corrosion-resistant species implanted bulk metal is composed of at least about three percent of the oxide of the corrosion-resistant species. Patent Application No. 70918